

EPA-600/R-93-044  
March 1993

EPA Region 5 Records Ctr.



299692

## **FINAL REPORT**

# **CHARACTERIZATION OF EMISSIONS FROM THE SIMULATED OPEN-BURNING OF NON-METALLIC AUTOMOBILE SHREDDER RESIDUE**

Prepared by:

**Jeffrey V. Ryan and Christopher C. Lutes**

**Acurex Environmental Corporation  
4915 Prospectus Drive  
P.O. Box 13109  
Research Triangle Park, NC 27709**

**EPA Contract No. 68-DO-0141  
Technical Directive Nos. 91-030/92-055**

**EPA Project Officer: Paul M. Lemieux**

**Air and Energy Engineering Research Laboratory  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711**

**Prepared for:  
U.S. Environmental Protection Agency  
Office of Research and Development  
Washington, D.C. 20460**

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2-1. Diagram of Burn Hut . . . . .	5
2-2. Aerial View of PIC Facility . . . . .	6
2-3. Sampling Systems in Sample Shed . . . . .	7
2-4. PM <sub>10</sub> Medium Volume Particulate Sampler . . . . .	19
3-1. Burn Rates of Fluff . . . . .	22
3-2. Temperatures Over Burn Pit . . . . .	23
3-3. CO Concentrations in Three Fluff Tests . . . . .	24
3-4. CO <sub>2</sub> Concentrations in Three Fluff Tests . . . . .	25
3-5. THC Concentrations in Three Fluff Tests . . . . .	26
3-6. NO Concentrations in Three Fluff Tests . . . . .	27
3-7. Total Volatiles Vs. Burn Rate . . . . .	29
3-8. Estimated Emissions for Selected CAAA HAPs . . . . .	32
3-9. PAHs in the Vapor Phase . . . . .	44
3-10. PAHs in the Particulate Phase . . . . .	45
3-11. Estimated Emissions for Vapor Phase PCDDs/PCDFs . . . . .	47
3-12. Estimated Emissions for Particulate-bound PCDDs/PCDFs . . . . .	48
3-13. Total PCDD/PCDF Estimated Emissions . . . . .	49
3-14. Estimated Emissions for Selected Metals . . . . .	51
3-15. Distribution of Organics by Sampling Method . . . . .	54
3-16. Distribution of Organics by Boiling Point . . . . .	55
3-17. Particle Mass Distribution . . . . .	57

## SECTION 1

### INTRODUCTION

The reclamation process for retrieving recyclable ferrous and non-ferrous metals from scrap automobiles generates a non-metallic waste product called "fluff." The fluff waste stream from automobile reclamation facilities also often includes the non-metallic residue of major household appliances which are known as "white goods".<sup>1</sup> The major constituents of fluff are plastics such as polyethylene (PE), polypropylene (PP), acrylonitrile-butadiene-styrene (ABS), polyurethane foam (PUF), polyvinylchloride (PVC), rubber, glass, wood products, cloth, paper, dirt, and electrical wiring.<sup>2,3</sup> The actual composition of fluff depends on the type of separating technique used during the reclamation process. In one such process, the fluff is separated from the desired, recyclable material using a series of air blowers and yields the final waste product described above. Another common reclamation technique uses water to separate floating, undesirable products from the denser material.<sup>4</sup> With this process, the denser materials such as glass and electrical wiring are less likely to be present in the fluff fraction.

In 1974, Mahoney et al., reported that a large percentage of automotive plastics are processed at approximately 100 junk automobile shredders in this country. These reclamation facilities are capable of processing 50,000-200,000 automobiles per year.<sup>5</sup> Valdez et al., state that more than half of the automobiles scrapped annually in the United States are now processed by shredding.<sup>2</sup> Since 1960, the amount of plastic contained in automobiles has increased drastically, and this trend is projected to continue. The average automobile contains more than 90 kg (200 lb) of plastics.<sup>6</sup>

## **SECTION 2**

### **EXPERIMENTAL APPROACH**

#### **2.1 GENERAL PROJECT DESCRIPTION**

The project consisted of a replicate study to collect and qualitatively and quantitatively characterize organic and inorganic emissions resulting from the simulated open combustion of actual automobile fluff. Small quantities (9.1-11.4 kg [20-25 lb]) of fluff were combusted in test facilities specifically designed to simulate open-combustion conditions. The tests were conducted in triplicate to allow for the heterogeneous composition of the fluff and to assess reproducibility. A portion of the combustion effluent was diverted to an adjacent sampling facility via an induced draft duct. Organics were collected using the volatile organics sampling train (VOST) and a semivolatile organics/particulate collection system using XAD-2 and particulate filters. Metal aerosols were collected on particulate filters. The organic constituents were analyzed both qualitatively and quantitatively using gas chromatograph/mass spectrometer (GC/MS), gas chromatograph/flame ionization detector (GC/FID), and gravimetric methodologies. The metal aerosols were characterized using an inductively coupled argon plasma (ICAP) method. Measured concentrations were related to dilution air volumes and measured net mass of fluff combusted to derive emission rates.

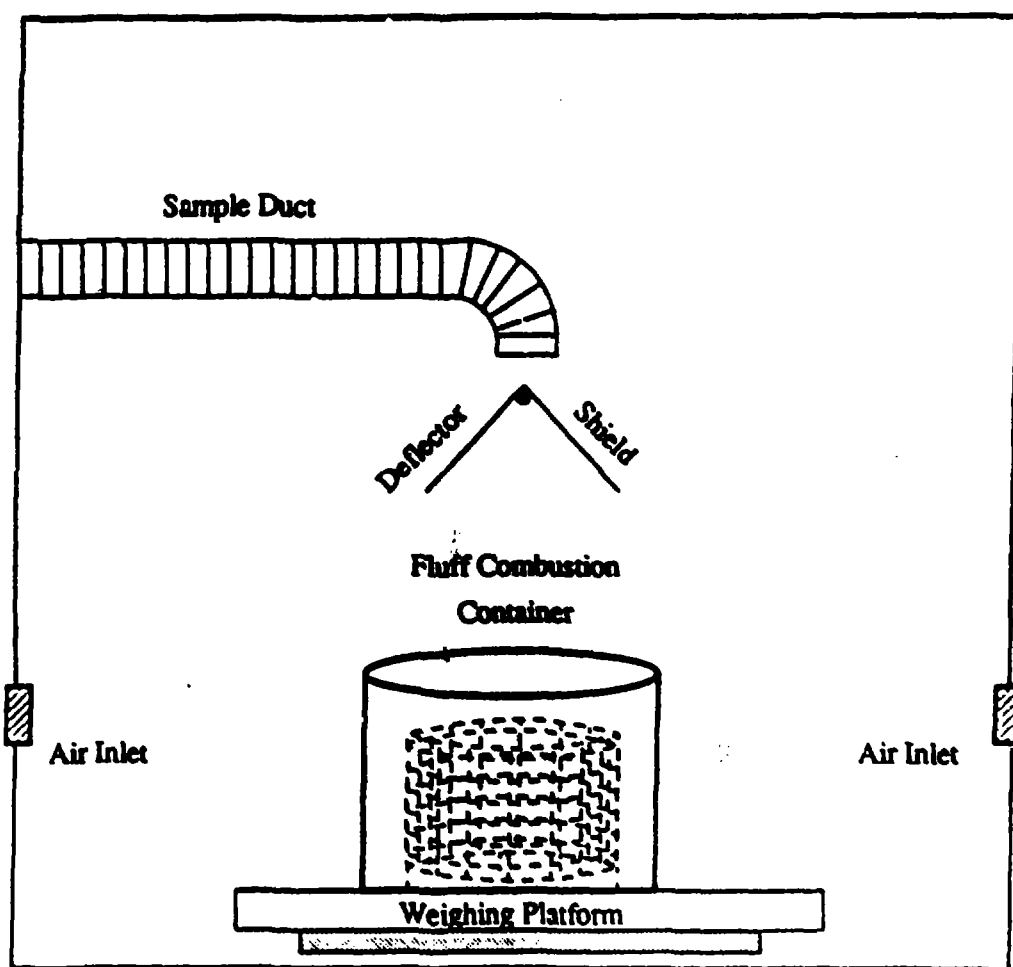


Figure 2-1. Diagram of burn hut.

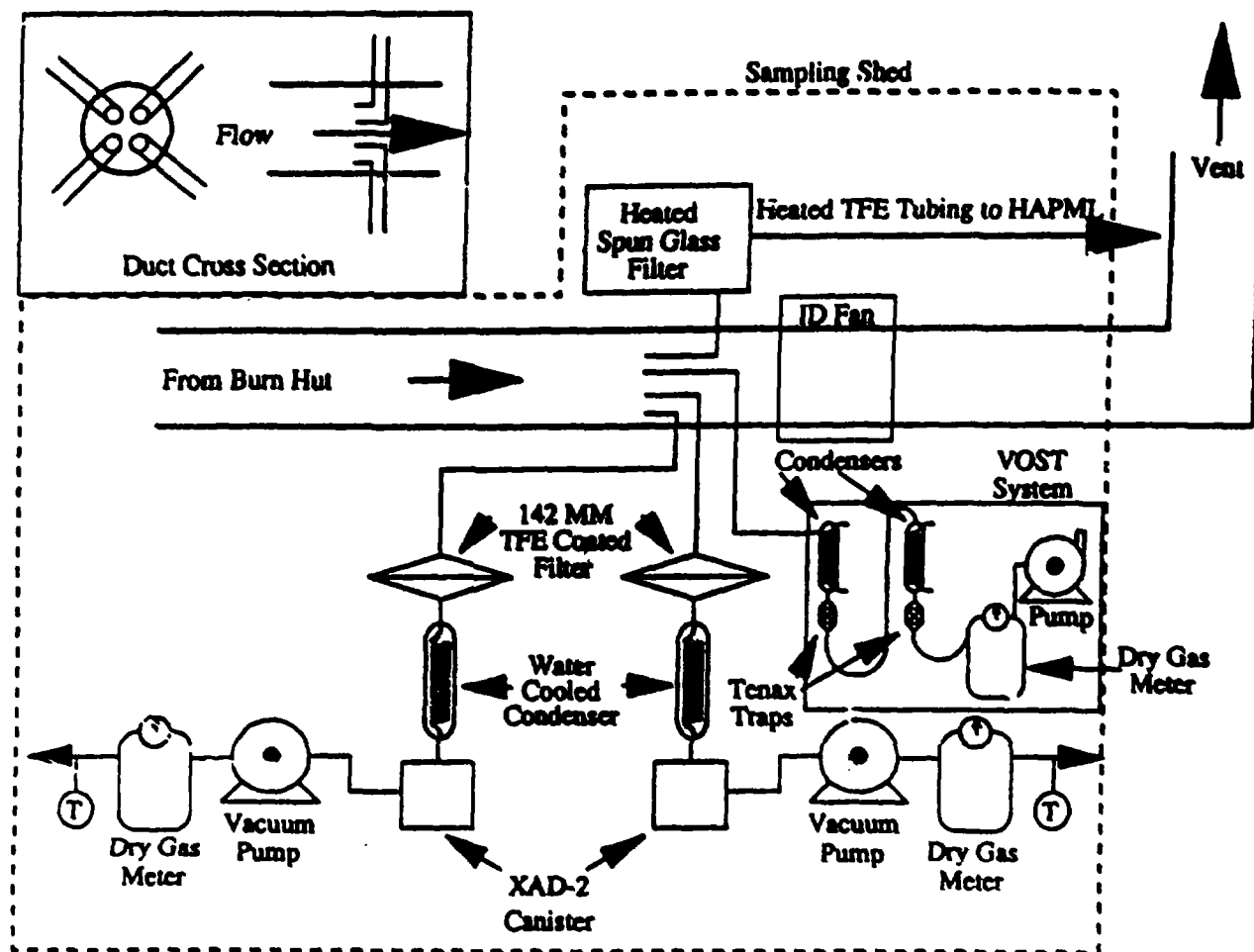


Figure 2-3. Sampling systems in sample shed.

A visual inspection of the as-received test material confirmed the presence of polyurethane foam, various unknown plastics, coated and uncoated electrical wiring, compressed wood products, and metal fragments. The fluff was combusted in a 0.61 m (24 in) x 0.56 m (22 in) diameter cylindrical, steel vessel.

The fluff was contained in a wire mesh support placed within the combustion vessel. The wire mesh support was used to allow adequate oxygen access within the combustion vessel. Nominally, 11.4 kg (25 lb) of fluff was placed into the combustion apparatus for each of the three tests. Before fluff ignition, the CEMs were operated for at least 15 min to establish background levels. During this time, the conditioned air handling system was operating and continued to operate throughout the test period.

After the baseline levels had been established, the fluff was manually ignited with a propane torch. After 1-2 min, the torch was removed, and the burn hut door closed to leave a 102-mm (4-in) opening for visual observation. After 5-15 min from the time the fluff was ignited, to allow sufficient time for any propane combustion products to dissipate, the metal, dioxin, and organic semivolatile sampling systems were activated. The volatile organic sampling train (VOST) was operated for three separate intervals during each test to characterize volatile organic emissions under various fluff combustion conditions. At the start and end of each sample condition, as well as continuously throughout the duration of the test, the time and net weight of fluff in the combustion pit were recorded digitally. Temperatures inside the burn hut (over the burn pit, at the deflector shield, and at the entrance to the transfer duct), within the sample duct (in the burn hut and in the sample shed), and dilution air temperatures were digitally recorded continuously throughout the duration of the test.

In addition to these three tests, a "hut blank" test was conducted between the second and third actual tests. In this experiment, the test facility and sampling apparatus were operated as in an actual test but no fluff was combusted. The purpose of this test was to assess the background levels of

tube set was installed in the sampling train and sampled. A laboratory blank sample was also analyzed. All samples were analyzed within 30 days of collection.

The VOST samples were analyzed by GC/MS/FID on a purge-and-trap thermal desorption system. The effluent of the chromatographic column was split to each of the GC detectors for simultaneous detection of eluting analytes from one sample. Method 5040 of SW-846 best represents the procedure used for sample analyses.<sup>11</sup> Compound identifications were accomplished using multicomponent calibration standard comparisons, mass spectral library searches as well as investigator interpretation. Identified analytes were quantified using GC/MS or GC/FID system responses. The system selected for quantification was based on the characteristics of the compound identified.

Before calibrating the analysis of samples, the MS was tuned with perfluorotributylamine (PFTBA) to linearize the MS over the total ion monitoring range of mass units (24-300 amu). The MS was calibrated with a variety of volatile compounds, determining relative response factors between the internal standard, D<sub>6</sub>-benzene, and the analyte of interest. A continuing calibration standard containing known concentrations of acrolein, toluene, cyclohexane, hexanol, decane, D<sub>6</sub> benzene, and bromofluorobenzene (BFB) was analyzed daily to verify acceptable system performance. The FID was calibrated by determining the linear response to varied concentrations of toluene containing standards.

The Tenax<sup>®</sup> and Tenax<sup>®</sup>/charcoal samples were desorbed in a clamshell heater maintained at 220 °C, purging the organics for 10 min with helium at a nominal flow rate of 10 mL/min onto a cryogenically cooled (0 °C) Tenax<sup>®</sup> trap. The tubes were analyzed in pairs and desorbed in reverse direction from that sampled. The Tenax<sup>®</sup> trap was ballistically heated to 250 °C, and the carrier directed onto a 30-m x 0.32-mm x 1.8- $\mu$ m film thickness DB-624 megabore column (J & W Scientific). The column head pressure was 8 psig. The GC oven temperature was cryogenically maintained at 0 °C for 5 min; then a temperature ramp was invoked at 3 °C/min until reaching 250 °C, where the temperature was held for 5 more min. As the sample constituents eluted from the

#### **2.3.4 Semivolatile Organics and Particulate Matter**

Semivolatile organics and particulate matter were collected using a sample system modified for use in this study to operationally separate semivolatile organics into gaseous and particulate-bound fractions. A 0.95 cm (3/8-in) OD stainless steel tube connected the sampling manifold to a particulate filter assembly. Particulate was collected on a 142-mm diameter Teflon<sup>®</sup>-coated, glass fiber filter in the filter housing. An ice water-cooled condenser was located between the filter assembly and the XAD-2 sorbent module to cool the sample gas stream before contact with the XAD-2. The exit of the sorbent module was connected to a pump and metering system. The gaseous sample was collected at an average flow rate of 17.0-34.0 L/min (0.6-1.2 scfm) for approximately 3 h.

Two separate semivolatile organic/particulate collection systems were operated simultaneously during the test period. One sample system was used to collect samples for the purpose of general semivolatile organic and particulate characterization while the remaining system was used to collect samples for polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) analyses. The only difference in operation between the two trains is the type of XAD-2 sorbent module used to collect semivolatile organics. The stainless steel XAD-2 sorbent module used in the general organic sampling system contained approximately 150 g of XAD-2 while the ice water-cooled glass XAD-2 module used for PCDD/PCDF collection contained approximately 40 g. Field and laboratory blanks were collected for the general organic train and a field blank was collected for the dioxin train. Field blanks consisted of filter and XAD-2 samples transported to the test facility along with the actual samples. The laboratory blank consisted of a filter or XAD-2 module retained in the analytical laboratory.

The Teflon<sup>®</sup>-coated, glass fiber filters used for particulate collection were desiccated, tared, and placed in aluminum foil and a zip-lock bag before use. After sample collection, the particulate samples were stored desiccated, weighed, and stored at 4 °C until extraction. Cleaned and quality control checked (QC'd) XAD-2 resin was placed in sealed modules, sealed in teflon bags, and stored

using an alkane mix standard. The  $C_7$ ,  $C_{10}$ ,  $C_{12}$ ,  $C_{14}$ ,  $C_{17}$  n-alkane mix was used to establish the boiling point retention window as well as the system response. All peaks with retention times falling between, but not including, the  $C_7$  and  $C_{17}$  retention times, were quantified. The system response to the  $C_{10}$ ,  $C_{12}$ , and  $C_{14}$  alkanes was used for quantification. The analysis was performed using a 30-m x 0.25-mm x 0.25- $\mu$ m film thickness DB-5 column (J & W Scientific). For the XAD-2 samples, the 1- $\mu$ L injection was made with the oven temperature held at 40 °C for 3 min, ramped to 250 °C at 14 °C/min, and held for 5 min after reaching final temperature. For the filter samples, the 1- $\mu$ L injection was made at 40 °C, which was held for 3 min. The oven was then ramped at 14 °C/min to 170 °C. The temperature was then ramped at 4 °C/min to 255 °C then at 2 °C/min to 300 °C where it was held for 2 min. A separately prepared quality control standard was injected at the beginning and end of each analytical day to verify instrument performance.

The GC/MS data were acquired on a system configured for capillary column use. A 30-m x 0.32-mm x 0.25- $\mu$ m film thickness DB-5 column (J & W Scientific) was directly interfaced to the MS source (interface temperature = 300 °C). Before calibrating or analyzing the samples, the MS was tuned with perfluorotributylamine (PFTBA). Continuing calibration standards were injected at the beginning and end of each analytical day to verify the consistency of instrument performance. Injections of 1-2  $\mu$ L were made into a splitless injector maintained at 300 °C. The XAD-2 and particulate fractions were analyzed using different temperature programs. The XAD-2 fractions were analyzed with the initial oven temperature of 40 °C maintained for 3 min. The oven temperature was then ramped at 5 °C/min to 300 °C and held for 5 min. The particulate fractions were analyzed with the initial oven temperature of 40 °C maintained for 3 min, at which time the temperature was ramped at 14 °C/min to 170 °C. The temperature ramp was changed to 4 °C/min until reaching 255 °C, at which time the temperature ramp was changed to 2 °C/min until reaching 300 °C where the temperature was maintained an additional 2 min.

levels and response factors from each level were averaged. The MS was calibrated with PFTBA and a continuing calibration standard was run at the beginning of each analytical day. The mass spectrometry was performed in the selected ion monitoring mode using the parent ( $M^+$ ) ion for quantification and the ( $M+1^+$ ) ion for confirmation of analyte identification.<sup>13</sup>

The PCDD/PCDF samples were analyzed by a hybridized method utilizing techniques found in SW-846 Method 8280 and 40 CFR Part 60, Appendix A, Method 23.<sup>14,15</sup> The samples were analyzed by low resolution GC/MS where isotopically labeled homologues for all congeners were used for qualitative and quantitative purposes. The analytical method used does not identify individual isomers within each congener group but does, however, quantify each isomer chromatographically resolved within each congener group. The data are reported here in terms of the total analytical concentration within each congener group.

### 2.3.5 Metal Aerosols

Particulate matter containing metal aerosols was collected using a separate sampling system to characterize airborne metals emissions. A gaseous sample was drawn across a 142-mm diameter quartz fiber filter under vacuum at an average flow rate of 17.0-42.5 L/min (0.6-1.5 cfm) for about 3 h. The quartz filters used were desiccated and tared, then placed in aluminum foil and a zip-lock bag before use. A field blank sample, consisting of a filter transported to the test facility along with the actual samples, was also obtained. Following sample collection, the samples were again desiccated and weighed. Ultimately, the samples were delivered to a contracted analytical laboratory for metals quantification. Metals potentially present in fluff samples were chosen for quantification. The samples were analyzed by inductively coupled argon plasma (ICAP) for aluminum, arsenic, barium, cadmium, total chromium, copper, lead, magnesium, selenium, and zinc.<sup>16</sup>

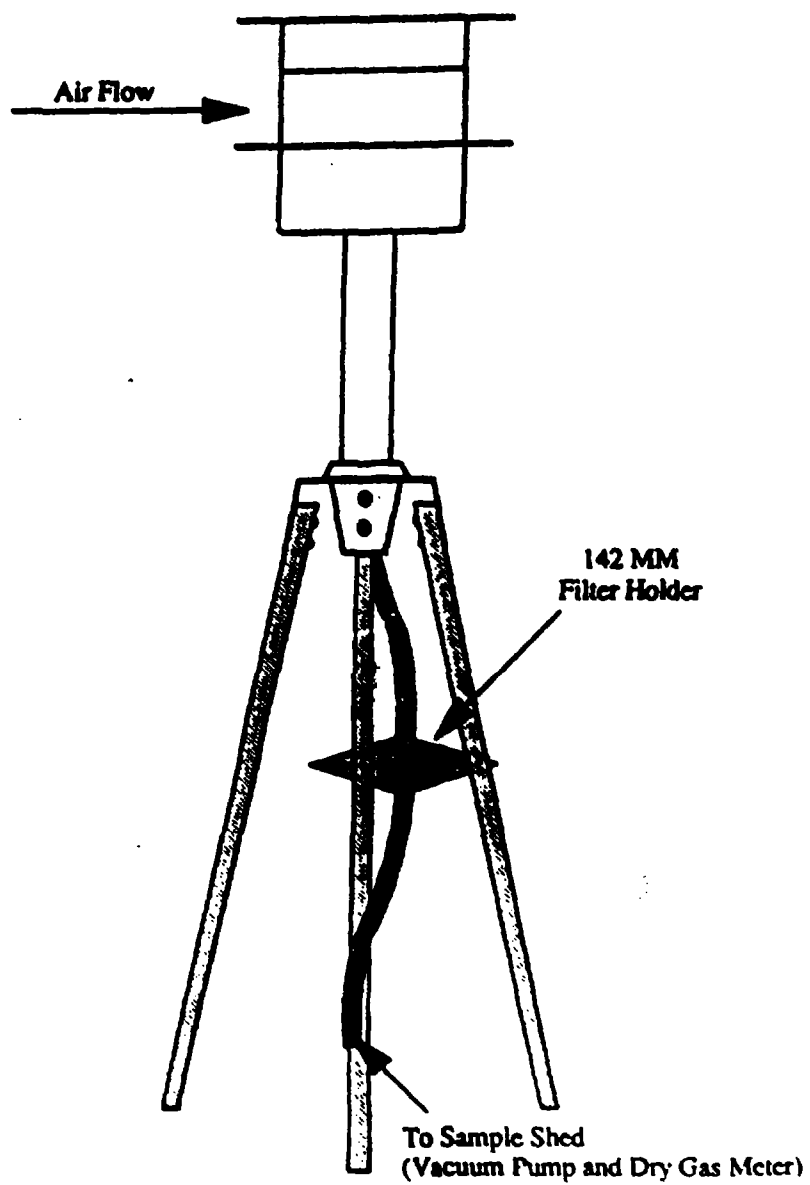


Figure 2-4. PM<sub>10</sub> medium volume particulate sampler.

**TABLE 3-1. COMBUSTION CONDITIONS IN THREE FLUFF TESTS**

	Day 1	Day 2	Day 3
Mass fluff at start (kg)	11.3	10.7	11.2
Weight after 200 min of combustion (kg)	5.8	5.8	6.2
Fluff mass lost because of combustion in 200 min (%)	48.7	45.8	44.6
Average burn rate over 200 min test (kg/hr)	1.65	1.47	1.50
Average burn rate over sampling period (kg/hr)	1.56	1.50	1.50
Length of sampling period (min)	180	183	174

Total mass of fluff combusted was determined by subtracting the final mass of material in the test apparatus from the initial mass. The net mass of fluff combusted divided by the duration of the test period determined the average burn rate for each test. Table 3-1 also presents the average burn rate of fluff for each 3-h test. Given the non-homogeneity of the composition of the fluff, there is excellent agreement (less than 20 relative percent difference) between the average burn rates of the three tests.

Burn rates were also determined for smaller elapsed periods of time. Burn rates were determined by relating the mass of fluff combusted to the length of time the mass was burned. Figure 3-1 represents the burn rates relative to elapsed time for each of the three tests. Maximum burn rates were observed within 20 min of material ignition. After this time, burn rates gradually decreased throughout the burn. Figure 3-2 presents the temperatures observed by a thermocouple placed directly over the combustion apparatus. Peak temperatures correlate well with peak burn rates.

Figures 3-3 to 3-6 present the continuous emissions monitoring data for CO, CO<sub>2</sub>, THC, and NO, respectively. Peak concentrations correlate reasonably well with peak burn rates. However, the THC data reveal peak emissions at periods farther into the test than the observed peak burn rates. The oxygen data are not presented graphically. Over the course of the burns, O<sub>2</sub> concentrations remained greater than 19 percent indicating that conditions adequately simulated an open combustion environment where combustion would not be expected to be oxygen starved. For purposes of clarity,

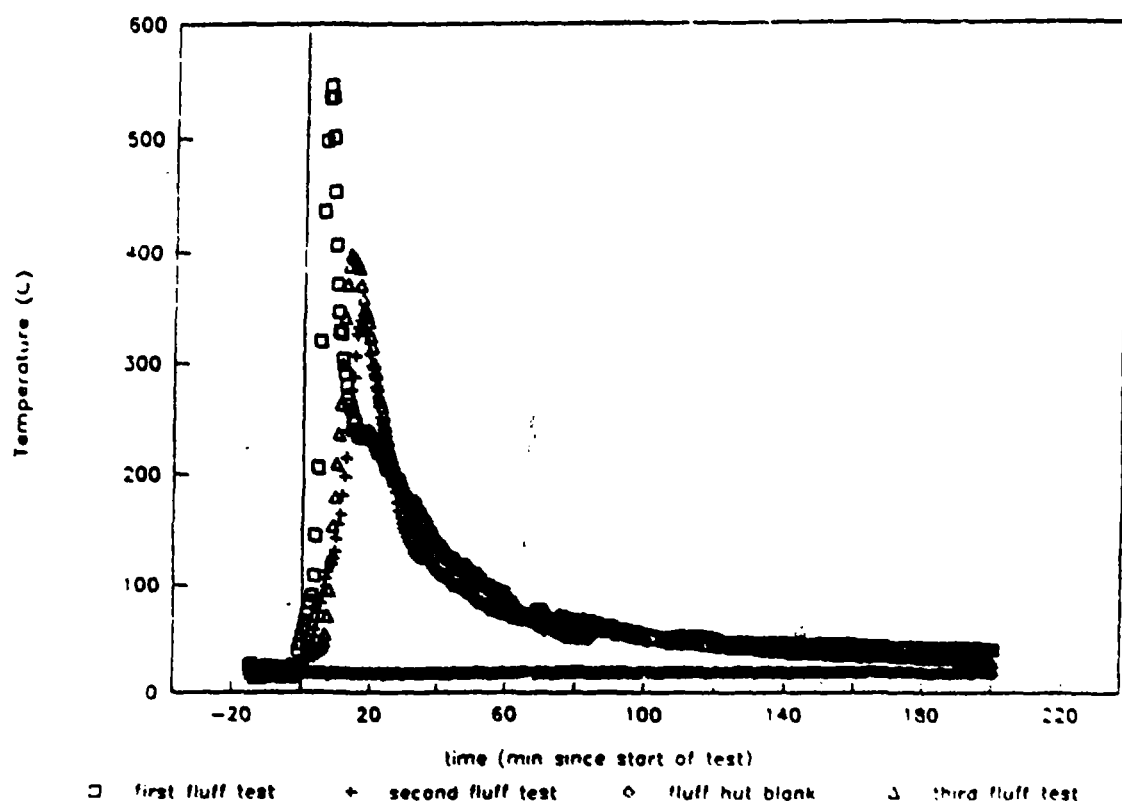


Figure 3-2. Temperatures over burn pit.

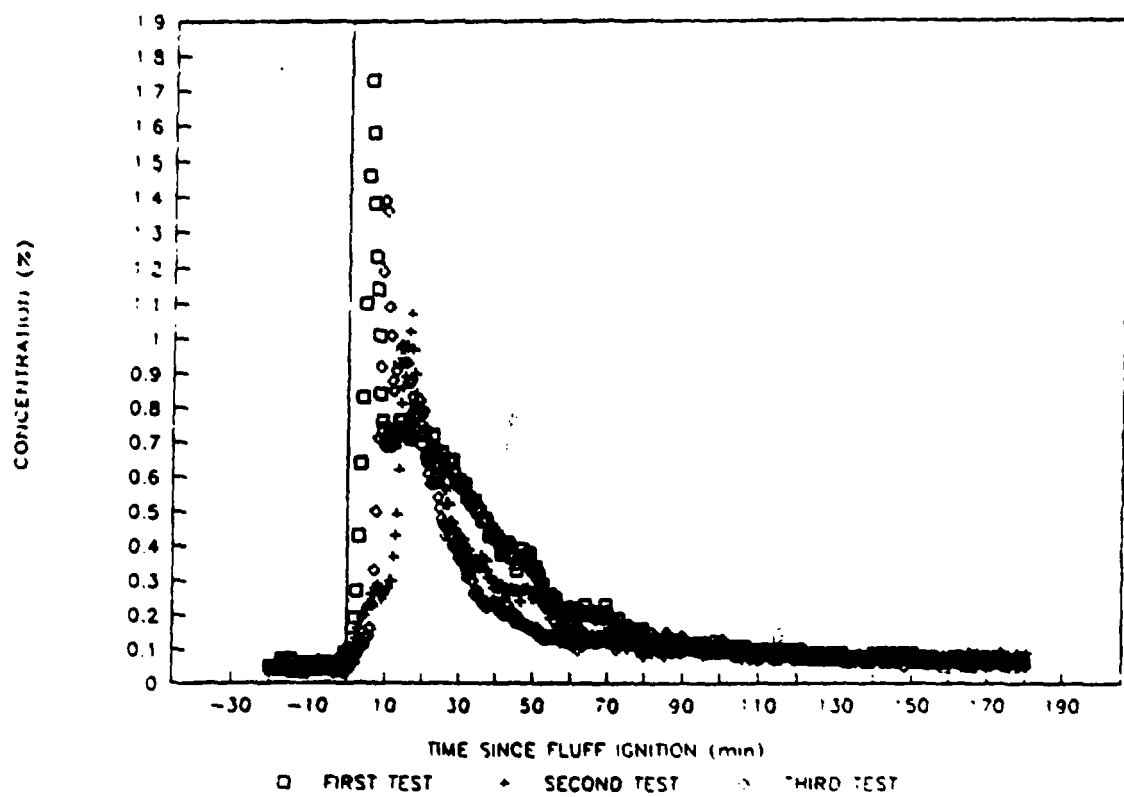


Figure 3-4. CO<sub>2</sub> concentrations in three fluff tests.

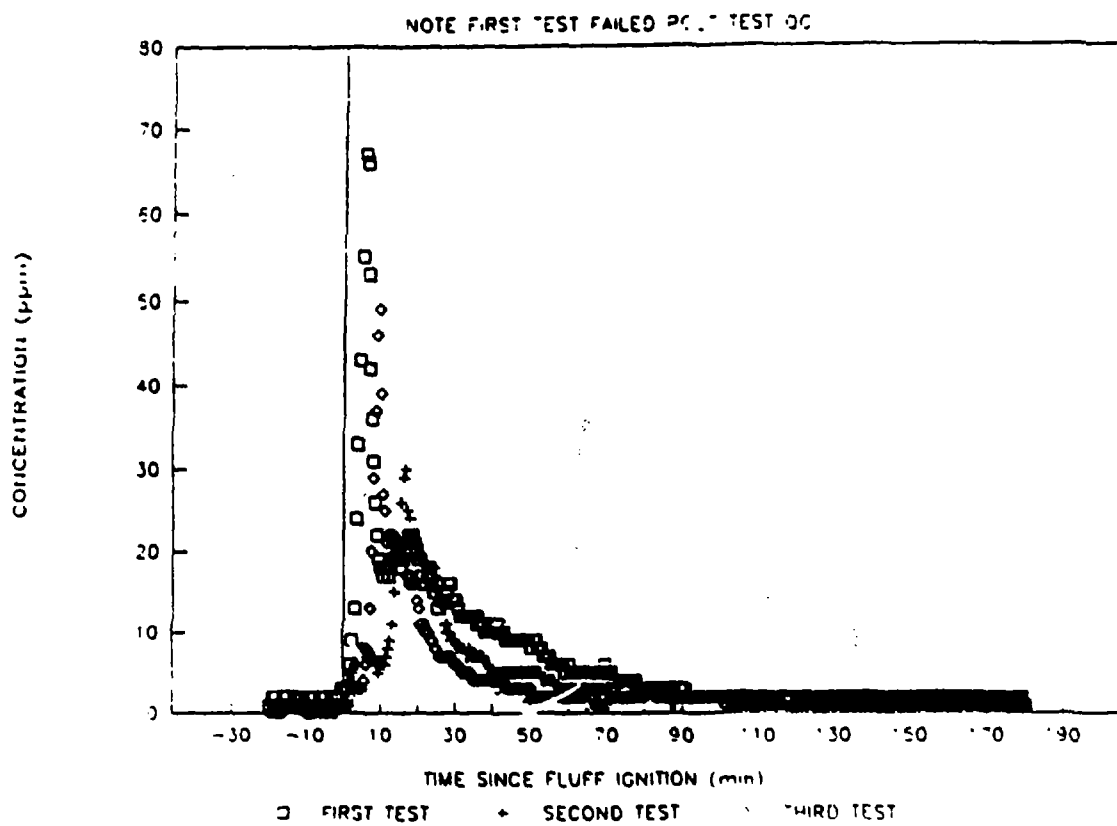
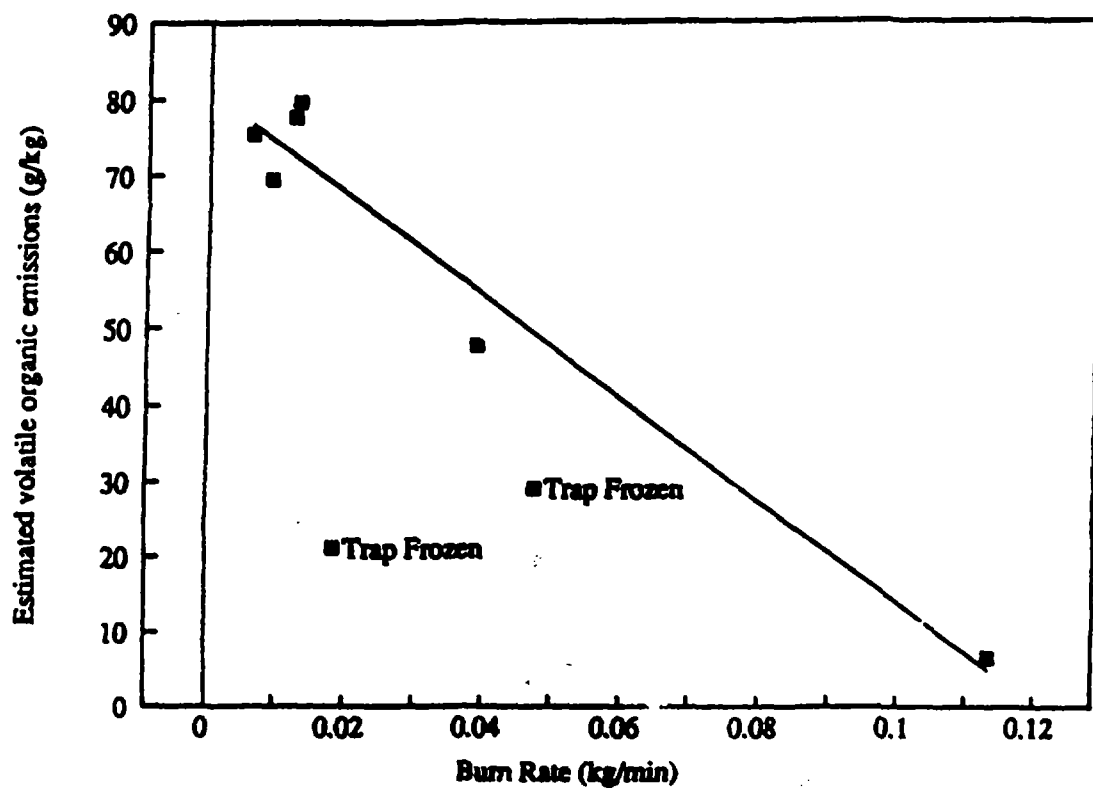


Figure 3-6. NO concentrations in three fluff tests.



**Notes:**

Linear regression does not include samples in which trap freezing was noted.

Linear regression  $r^2 = 0.959$ .

Figure 3-7. Total volatiles vs. burn rate.

determined by dividing the mass collected by the volume sampled, was multiplied by the volume of air added to the burn hut per unit time. This represents the mass of organic material emitted per unit time. Dividing by the respective sluff burn rate yields the mass of volatile organics emitted relative to the mass of sluff combusted.

Table 3-3 presents emissions data for selected individual compounds identified in the VOST samples, and Table 3-4 presents a list of all individual compounds tentatively or positively identified in VOST samples. Emphasis was placed on establishing emissions data for compounds found on the Clean Air Act Amendment (CAAA), Title III, Hazardous Air Pollutants (HAP) list. Figure 3-9 graphically depicts the major volatile organic compounds (VOCs) found on this list and their relative contributions. Benzene is one of the top two volatile organic compounds emitted, generating nearly 10 g for every kilogram of sluff consumed in combustion. Benzene is also one of the more toxic compounds identified.

A comparison of the total VOC mass to the mass of individually identified compounds with boiling points within this range, indicates that greater than 70 percent of the detectable mass has been characterized. The remaining fraction was not identified because of the complexity of the sample, limitations of the analytical system, and budgetary constraints.

Very few detectable peaks were seen in the field and laboratory blank samples. Compounds present in field and laboratory blanks included methylene chloride, acetone, trichlorofluoromethane, toluene, and benzaldehyde. All compounds present in these blanks were either not present or present at more than an order of magnitude greater concentration in the actual samples. The compounds that were detected at low concentrations in the blanks but not in the samples may well have been also present in the samples but obscured by interfering analytes at much higher concentrations.

TABLE 3-3. ESTIMATED EMISSIONS FOR SELECTED VOLATILE ORGANICS (continued on next page)  
(g Pollutant/kg Fluff combusted)

Pollutant	Identification confirmed by comparison to standard?	Test 1 Sample 1	Test 1 Sample 3	Test 2 Sample 1	Test 2 Sample 2	Test 3 Sample 2	Test 3 Sample 3	Test 1 Avg.	Test 2 Avg.	Test 3 Avg.
ACETALDEHYDE	NO	0.315	0.437	1.295	1.507	1.016	ND	0.376	1.401	0.508
n-Pentane	NO	ND	7.481	2.052	5.191	4.700	3.955	3.741	3.622	4.328
ACROLEIN	YES	0.258	1.437	1.044	3.220	2.344	1.766	0.848	2.132	2.055
ACETONITRILE	NO	0.106	0.416	0.441	0.000	0.964	2.900	0.261	0.221	1.932
ACRYLONITRILE	NO	0.304	0.558	0.886	0.714	0.912	1.260	0.431	0.800	1.086
C5H6O Methyl Furan	NO	ND	ND	0.076	0.113	0.137	ND	0.000	0.095	0.068
BENZENE	YES	2.846	9.989	9.138	9.811	9.083	16.635	6.417	9.475	12.859
1-Heptene	NO	ND	1.485	0.695	1.572	1.395	0.862	0.743	1.134	1.128
n-Heptane	YES	ND	1.019	ND	1.076	0.944	0.720	0.510	0.538	0.832
C5H8O2, Carboxylic Acid, Methyl Ester	NO	0.007	ND	ND	0.072	ND	ND	0.003	0.036	0.000
TOLUENE	YES	0.564	6.634	4.739	8.626	8.674	34.920	3.599	6.683	21.797
n-Octane	YES	ND	ND	ND	NAV	0.999	0.725	0.000	0.000	0.862
C9H18 Trimethylcyclohexane	NO	ND	0.859	ND	NAV	0.542	0.365	0.429	0.000	0.454
CHLOROBENZENE	YES	0.053	0.966	0.891	NAV	1.851	5.176	0.510	0.891	3.513
ETHYL BENZENE	YES	0.076	4.086	2.188	NAV	4.242	15.974	2.081	2.188	10.108
m/p-XYLENE	YES	0.059	1.477	1.038	NAV	2.200	3.675	0.768	1.038	2.938
Styrene	NO	0.943	5.650	7.128	NAV	10.055	6.801	3.296	7.128	8.428
n-Decane	YES	ND	ND	ND	NAV	1.423	0.889	0.000	0.000	1.156
Benzaldehyde	YES	0.219	ND	ND	NAV	2.749	3.409	0.110	0.000	3.079

CAA HAPs listed in all cases

NAP = Not Applicable

NAV = Not Available

ND = Not Detected

TABLE 3-4. VOLATILE ORGANIC COMPOUNDS IDENTIFIED (continued on next page)  
(Listed in order of increasing retention time)

Compound Name or Class	Molecular Formula
Alkene	C <sub>4</sub> H <sub>8</sub>
Diene or Alkyne	C <sub>4</sub> H <sub>6</sub>
Alkene	C <sub>4</sub> H <sub>8</sub>
Diene or Alkyne	C <sub>4</sub> H <sub>6</sub>
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O
Alkene	C <sub>4</sub> H <sub>8</sub>
Alkene	C <sub>4</sub> H <sub>8</sub>
Alkene or Cyclic	C <sub>5</sub> H <sub>10</sub>
n-Pentane	C <sub>5</sub> H <sub>12</sub>
Alkene or Cyclic	C <sub>5</sub> H <sub>10</sub>
Diene	C <sub>5</sub> H <sub>8</sub>
Alkylated Cyclopropane	C <sub>5</sub> H <sub>10</sub>
Alkene	C <sub>5</sub> H <sub>10</sub>
2-Propenal (Acrolein)	C <sub>3</sub> H <sub>4</sub> O
Propanal	C <sub>3</sub> H <sub>6</sub> O
Diene	C <sub>5</sub> H <sub>8</sub>
Unsaturated Hydrocarbon	C <sub>5</sub> H <sub>8</sub>
Acetonitrile	C <sub>2</sub> H <sub>3</sub> N
Alkane	C <sub>6</sub> H <sub>14</sub>
Alkene	C <sub>6</sub> H <sub>12</sub>
2-Propenenitrile (Acrylonitrile)	C <sub>3</sub> H <sub>3</sub> N
Alkene or Cyclic	C <sub>6</sub> H <sub>12</sub>
Hexane	C <sub>6</sub> H <sub>14</sub>
2-Methyl-2-Propenal	C <sub>4</sub> H <sub>6</sub> O
Alkene	C <sub>6</sub> H <sub>12</sub>
Branched Alkene	C <sub>6</sub> H <sub>12</sub>
Alkene	C <sub>6</sub> H <sub>12</sub>
Methyl Furan	C <sub>5</sub> H <sub>6</sub> O
Diene or Alkyne	C <sub>6</sub> H <sub>10</sub>
Alkene	C <sub>7</sub> H <sub>14</sub>
Nitrile	C <sub>4</sub> H <sub>5</sub> N
Alkene Substituted Cyclic or Diene	C <sub>6</sub> H <sub>10</sub>
Substituted Cyclopropane	C <sub>7</sub> H <sub>14</sub>
Benzene	C <sub>6</sub> H <sub>6</sub>
Alkene	C <sub>7</sub> H <sub>14</sub>
1-Heptene	C <sub>7</sub> H <sub>14</sub>
n-Heptane	C <sub>7</sub> H <sub>16</sub>
Probably a Heptene	C <sub>7</sub> H <sub>14</sub>
Alkene	C <sub>7</sub> H <sub>14</sub>
Alkene	C <sub>7</sub> H <sub>14</sub>
Alkyne or Diene	C <sub>7</sub> H <sub>12</sub>
Alkene	C <sub>7</sub> H <sub>14</sub>
Alkene	C <sub>7</sub> H <sub>14</sub>
Carboxylic Acid, Methyl Ester	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>
Alkyl Substituted Cyclopentane	C <sub>8</sub> H <sub>16</sub>
Branched Alkane	C <sub>8</sub> H <sub>18</sub>

Few detectable peaks were seen in the hut blank samples. The compounds that were present, included dichlorodifluoromethane (Freon 12), allyl alcohol, propanol, methylene chloride, trichloroethane, 1,4-dioxane, and toluene. All compounds present in these blanks were either not present or present at more than an order of magnitude greater concentration in the combustion test samples. The one exception was a single sample (the second obtained during the hut blank test) in which toluene was detected at a level only a factor of two lower than the lowest sample toluene concentration (the third sample of the first combustion test). In summary, the volatile organic blank data support the validity of the sample data presented.

### 3.4 SEMIVOLATILE ORGANICS DATA

The characterization of semivolatile organic emissions collected on both the XAD-2 and particulate filters used an approach similar to that used to characterize the volatile organics emissions. TCO and GRAV analyses were performed separately on the XAD-2 and particulate filter extracts to determine total organic content based on boiling point range.

Table 3-5 provides a summary of these data expressed as estimated emissions. As expected, the XAD-2 sample fractions contained more chromatographable (vapor phase) mass than did the particulate filter fractions. Similarly, the particulate filter fractions contained more GRAV (condensable) mass than did the XAD-2 fractions. Of the total extractable semivolatile and non-volatile organic mass emitted, an average of 49.9 percent was contained on the XAD-2 fraction while the remainder was contained on the particulate. The TCO and GRAV values for the field, hut, and laboratory blanks were quite low compared to the sample values. No blank was greater than 21 percent of the lowest corresponding sample concentration.

GC/MS analyses were performed on each of the sample fractions to aid in identification of individual compounds. Table 3-6 lists the more than 45 compounds identified in the XAD-2 and particulate fractions. The compounds identified are similar to the types of compounds identified in the

TABLE 3-6. ESTIMATED EMISSIONS FOR ORGANIC COMPOUNDS COLLECTED ON XAD RESIN AND PARTICULATE FILTERS  
(Listed in increasing order of retention time) (continued on next page)

Compound	XAD Test 1	XAD Test 2	XAD Test 3	XAD Avg.	XAD Hot Blank	Particulate Test 1	Particulate Test 2	Particulate Test 3	Particulate Avg.	Particulate Hot Blank	Identification confirmed by comparison to known standards?	Quantification Method	Compound used for MS Rf's
ETHYL BENZENE	2.26	2.05	2.90	2.40	ND	ND	ND	ND	0.000	ND	YES	MS	Ethylbenzene
m,p-XYLENE	1.03	1.11	1.72	1.29	ND	ND	ND	ND	0.000	ND	YES	MS	p-Xylene
Ethynyl Benzene	0.38	0.39	0.61	0.46	ND	ND	ND	ND	0.000	ND	NO	FID	NA
STYRENE	6.27	6.49	11.81	8.19	ND	ND	ND	ND	0.000	ND	NO	FID	NA
1 Methyl 2-Pentyl Cyclopropane	0.46	ND	0.05	0.17	ND	ND	ND	ND	0.000	ND	NO	FID	NA
CYH12 Alkylated Benzene	0.95	1.05	1.13	1.05	ND	ND	ND	ND	0.000	ND	NO	FID	NA
Benzaldehyde	1.20	1.53	2.34	1.69	ND	ND	ND	ND	0.000	ND	YES	MS	Benzaldehyde
Ethyltoluene	0.07	0.12	0.22	0.14	ND	ND	ND	ND	0.000	ND	YES	MS	Ethylbenzene
Toluethylbenzene	0.17	0.17	0.09	0.14	ND	ND	ND	ND	0.000	ND	YES	MS	Toluethylbenzene
C7H12N Probably Benzoinitrile	3.51	3.78	ND	2.43	ND	ND	ND	ND	0.000	ND	YES	MS	Benzoinitrile
PHENOL	1.39	1.39	ND	0.99	ND	ND	ND	ND	0.000	ND	NO	MS	2-Ethyl-1-Hexanol
1,2 Dichlorobenzene	ND	0.17	0.15	0.11	ND	ND	ND	ND	0.000	ND	YES	MS	Dichlorobenzene
2-Ethyl-1-Hexanol	0.28	0.34	ND	0.21	ND	ND	ND	ND	0.000	ND	YES	MS	2-Ethyl-1-Hexanol
CYH8 Alkyl Substituted Benzene	0.40	0.44	0.78	0.54	ND	ND	ND	ND	0.000	ND	NO	FID	NA
Phenyltoluene	0.71	1.32	1.21	1.08	ND	ND	ND	ND	0.000	ND	NO	MS	Benzaldehyde
NAPHTHALENE	0.90	0.95	1.54	1.13	ND	ND	ND	ND	0.000	ND	YES	MS	Naphthalene
C12H24 Alkane or Cyclic	0.34	0.32	0.46	0.39	ND	ND	ND	ND	0.000	ND	NO	FID	NA
Dodecane	0.22	ND	0.28	0.17	ND	ND	ND	ND	0.000	ND	YES	FID	NA
Methylcyclohexanol	0.49	ND	0.31	0.26	ND	ND	ND	ND	0.000	ND	NO	MS	Ethylbenzene

CAAA HAPs listed in all caps  
NA = Not Available  
ND = Not Detected

TABLE 3-6. ESTIMATED EMISSIONS FOR ORGANIC COMPOUNDS COLLECTED ON XAD RESIN AND PARTICULATE FILTERS  
(Listed in increasing order of retention time) (concluded)

Compound	XAD Test 1	XAD Test 2	XAD Test 3	XAD Avg.	XAD Hls Blank	Particulate Test 1	Particulate Test 2	Particulate Test 3	Particulate Avg.	Particulate Hls Blank	Identification confirmed by comparison to known standards?	Quantification Method	Compound used for MS R/Fs
Torphenyl	ND	ND	ND	0.00	ND	0.050	0.070	ND	0.040	ND	NO	FID	NA
Dnocosane	ND	ND	ND	0.00	ND	0.112	0.118	0.1409	0.126	ND	YES	FID	NA
Tacosane	ND	ND	ND	0.00	ND	0.084	0.112	0.1348	0.113	ND	YES	FID	NA
Tetracosane	ND	ND	ND	0.00	ND	0.091	0.116	ND	0.069	ND	YES	FID	NA
C22H34O4 Benzene Dicarboxylic Acid	ND	ND	ND	0.00	ND	ND	ND	0.26	0.087	ND	NO	MS	Bis(2-Ethylhexyl)Phthalate
C24H38O4 Benzene Dicarboxylic Acid or Phthalate	ND	ND	ND	0.00	ND	ND	ND	0.156	0.052	ND	NO	MS	Bis(2-Ethylhexyl)Phthalate
1,28Benzenedicarboxylic Acid, Diheptyl Ester	ND	ND	ND	0.00	ND	ND	0.130	ND	0.043	ND	NA	NA	NA
Paracosane	ND	ND	ND	0.00	ND	0.111	0.096	ND	0.070	ND	YES	FID	NA
Bis(2-Ethylhexyl)Phthalate	ND	ND	ND	0.00	ND	0.761	1.995	2.418	2.058	ND	YES	MS	Bis(2-Ethylhexyl)Phthalate
Quaterphenyl	ND	ND	ND	0.00	ND	0.073	0.639	ND	0.057	ND	NO	FID	NA
Taonane	ND	ND	ND	0.00	ND	0.025	ND	ND	0.008	ND	YES	FID	NA

CAAA HAPs listed in all caps

NA = Not Available

ND = Not Detected

not detected in the actual samples or were at least an order of magnitude less concentrated than in the actual samples.

### 3.5 PAH ANALYSES

The results of PAH analyses conducted on the XAD-2 and particulate extracts by an independent laboratory are shown in Figures 3-9 and 3-10. These analyses confirm the emission of significant quantities of PAHs from the fluff combustion process. These analyses detected additional PAH compounds that were not detected in the GC/MS full-scan analyses, perhaps because of the presence of interfering compounds or the lesser sensitivity of full-scan methods as compared to selected ion monitoring methods. All 16 PAHs analyzed for were detected in at least some of the combustion experiments and most were detected in all three experiments. PAH concentrations in field, laboratory, and hut blanks were generally non-detectable and were, in no case, greater than 10 percent of the observed sample concentrations.

The vapor/particle distribution evidenced in these results shows the expected preponderance of lighter species in the vapor phase. For the analytes measured both in this analysis and in the general organic analyses, the level of agreement was encouraging. The estimated emissions for naphthalene agree quite closely in all three tests—within 30 percent relative percent difference—(see Table 3-6 and Figure 3-9) as would be expected because a compound specific MS response factor was used for naphthalene in the general organic analyses. There was less agreement for the other analytes reported in both data sets (acenaphthylene, phenanthrene, fluoranthene, and pyrene). This is not surprising, since the analytical methods differed greatly (GC/MS with selected ion monitoring vs GC/FID calibrated as TCO). However, a comparison of the values (see Table 3-6 and Figures 3-9,10) obtained in the two separate methods would suggest that quantification accurate to within one order of magnitude (the stated goal of the project) was obtained.

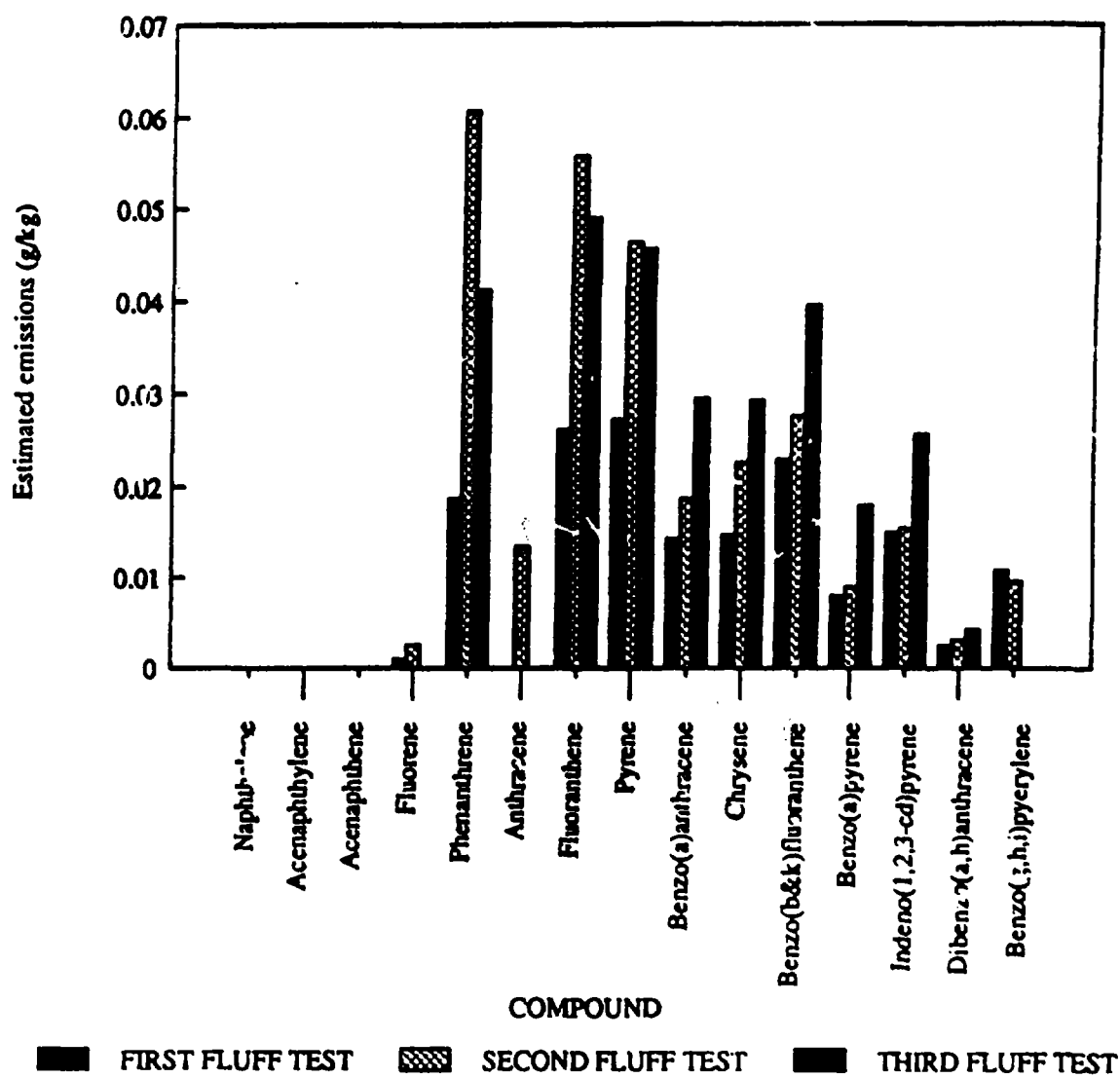


Figure 3-10. PAHs in the particulate phase.

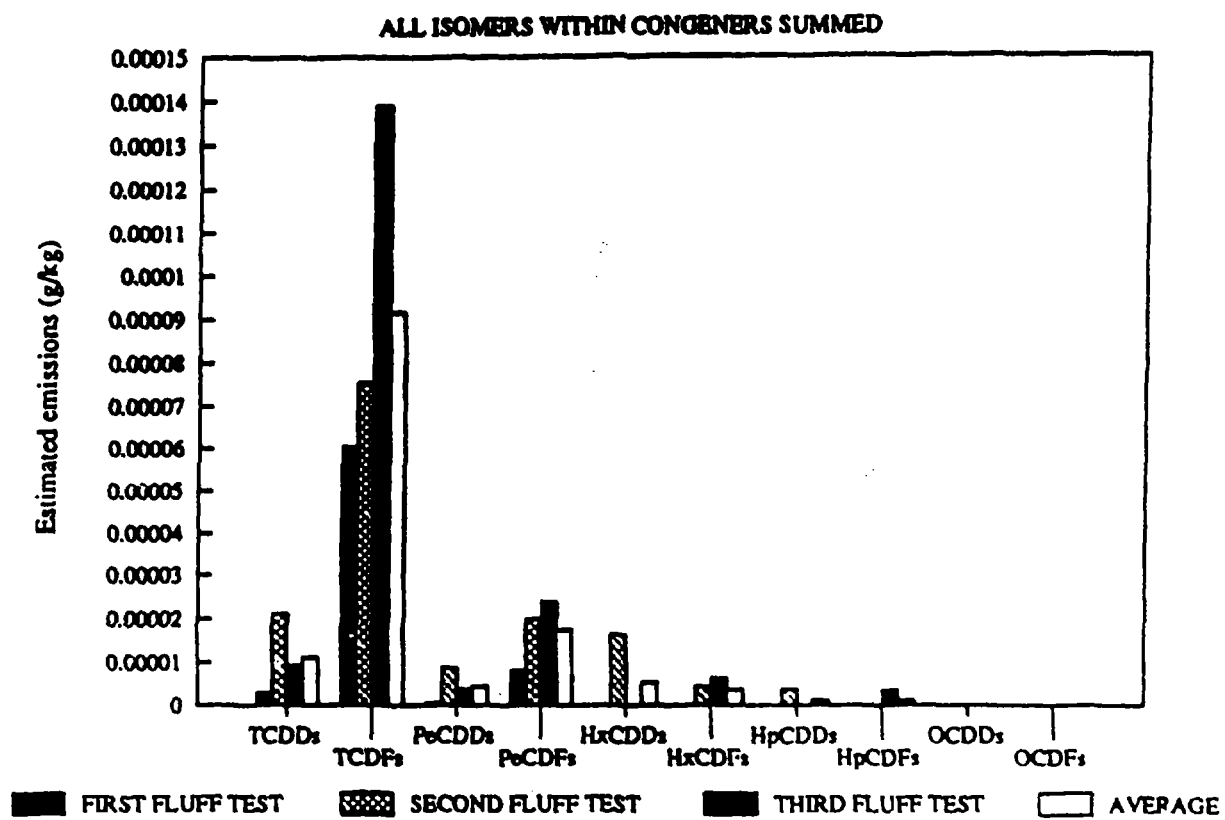


Figure 3-11. Estimated emissions for vapor phase PCDDs/PCDFs.

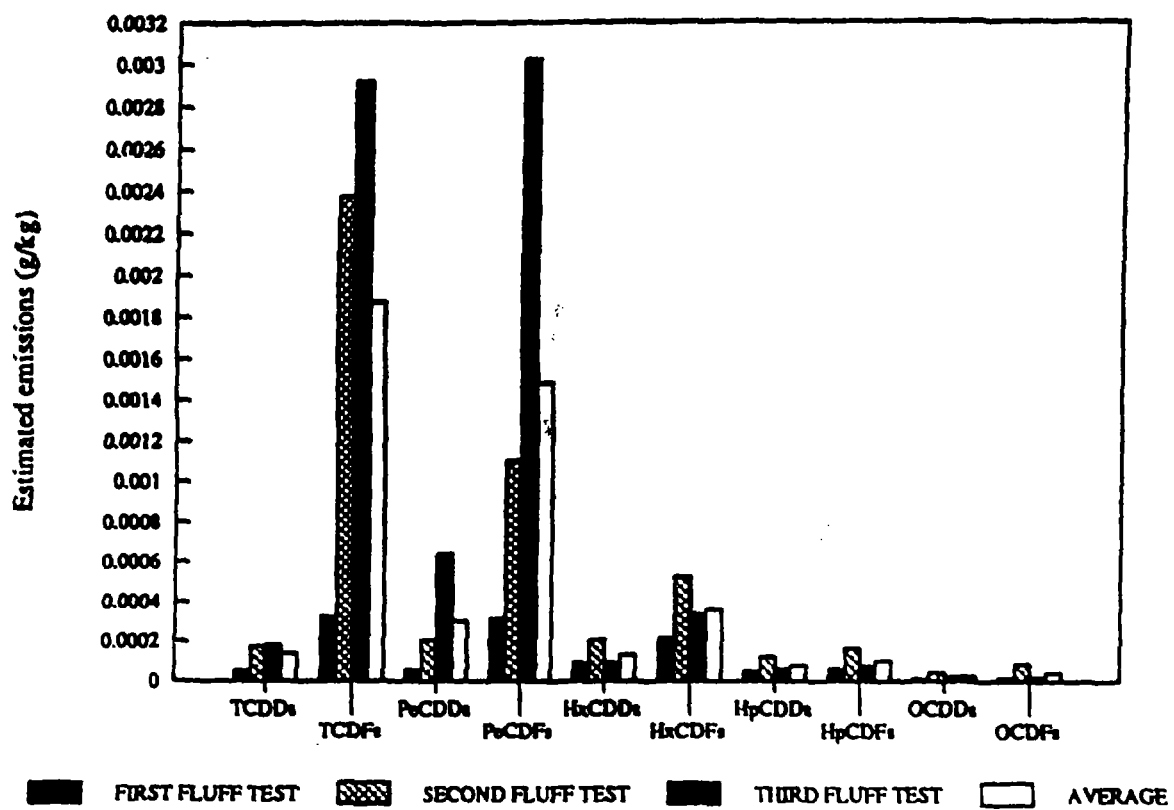


Figure 3-13. Total PCDD/PCDF estimated emissions.

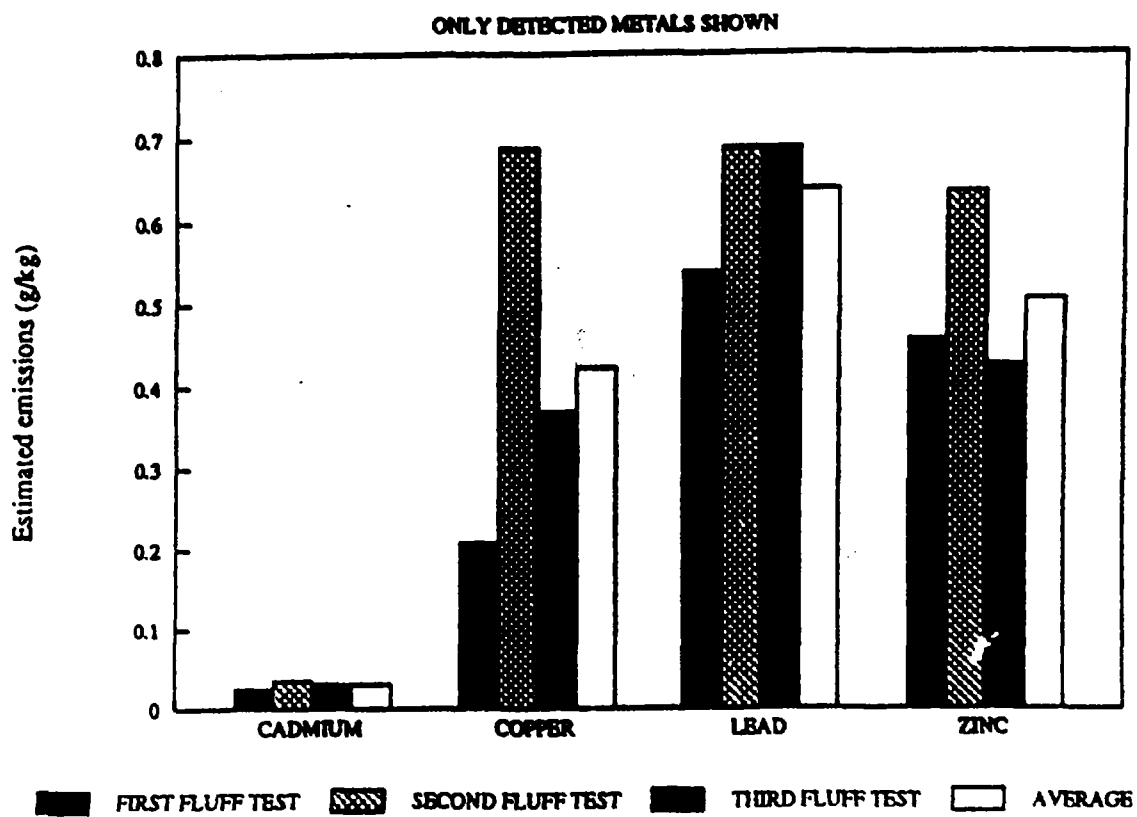


Figure 3-14. Estimated emissions for selected metals.

A separate medium vol 113 L/min (4 cfm) PM<sub>10</sub> ambient sampler was operated within the burn hut to characterize particulate matter 10  $\mu$ m in diameter and less. Because this sampling did not occur in a duct or stack, there is no concern with regards to isokineticity for these samples. The particulate matter emissions for this system are also presented in Table 3-8. For qualitative purposes, a comparison of the PM<sub>10</sub> to total particulate has been made based on total averaged values. The PM<sub>10</sub> comprises roughly 43 percent of the total particulate matter collected.

Levels of particulate collected in the hut, field, and laboratory blank samples collected were an order of magnitude less than the lowest values observed in actual test samples for the general organic, dioxin, and PM<sub>10</sub> trains. The metals train hut blank particulate concentration is 20 times less than any actual test sample and the field blank was 3.7 times less than the lowest test sample.

### 3.9 EMISSION DATA SUMMARY

The tests and subsequent analyses performed during this study were selected to characterize, as broadly as possible, the diverse emissions resulting from the open combustion of fluff. A considerable body of data were generated as a result. Because some approaches to understanding these data can be overwhelming and time consuming, the individual data sets have been summarized to illustrate their respective relative contributions to total mass emissions.

To assess the overall organic emissions, the volatile and semivolatile organics emission data were summarized. The total organics emitted, volatile (volatile determined using the FID response factor for toluene and totaling all compounds to but not including the retention time of toluene), vapor-phase semivolatile, and particulate-bound semivolatile, averaged more than 200 g/kg fluff combusted. The actual mass contribution from each fraction is summarized in Table 3-9. Figure 3-15 graphically presents the relative mass contributions of various sample fractions to the total organic mass emissions. Figure 3-16 depicts the relative mass distribution based on the boiling point of

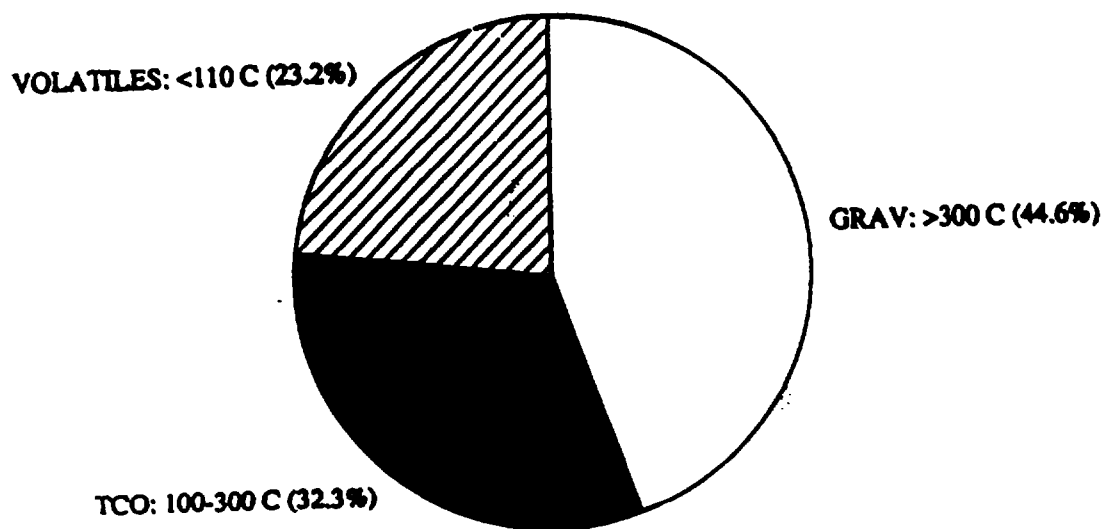


Figure 3-16. Distribution of organics by boiling point.

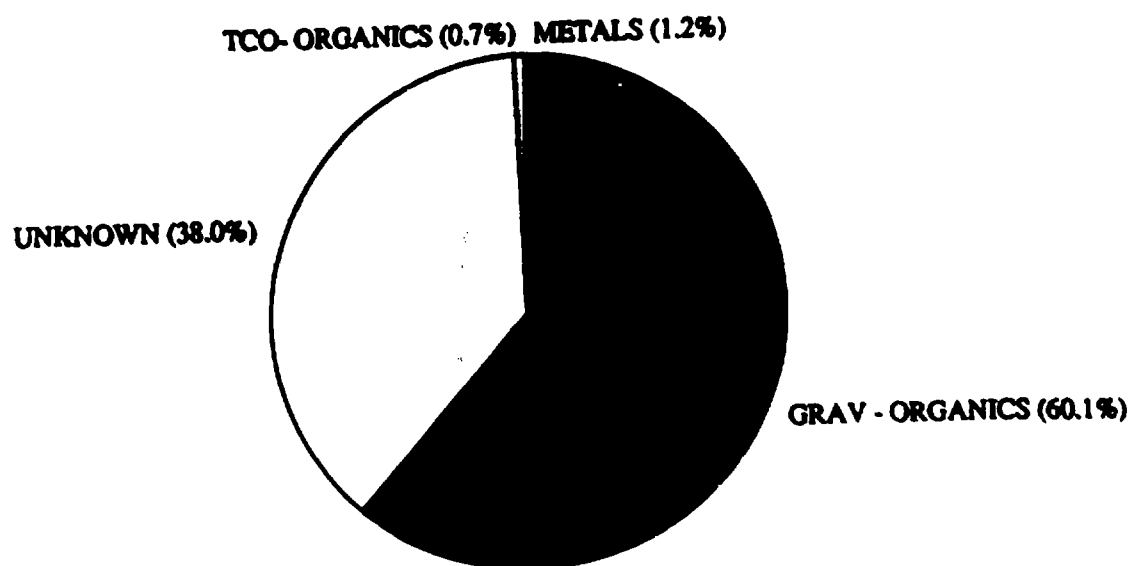


Figure 3-17. Particle mass distribution.

## SECTION 4

### SUMMARY AND CONCLUSIONS

This laboratory study successfully achieved its goals of characterizing the broad spectrum of emissions from open fluff combustion and of generating emission factors accurate to within one order of magnitude for these emissions. As previously discussed, the results from this study were used to perform a mass balance, the quality of which indicates that it is likely that the major emissions from this source have been detected by the sampling and analytical methods chosen. A large number of PICs have been identified, many of which are previously known products of combustion of various individual plastics. However, not all of the organic compounds present in the sample have been identified and quantified. The chromatograms obtained from these emissions samples were often highly complex, and all the chromatographically resolved peaks were not able to be identified especially in the semivolatile and particulate-bound organic fractions. The use of compound specific analytical methods, such as were used here for PCDDs/PCDFs, should reveal the presence of low but potentially significant concentrations of analytes not detected in this study. For example, given the prevalence of brominated flame retardants in commercial plastics and the identification of PCDDs and PCDFs in our sample, the production of the brominated analogues of PCDDs and PCDFs seems likely.<sup>28,29</sup> The use of bioassay directed fractionation in future studies of emissions from similar processes is suggested to determine if the unidentified organics are of any human health concern and to focus identification and quantification efforts.

emissions measured here for compounds of human health concern and the substantial quantities of combustible materials present in sluff landfills certainly merits a further evaluation of the risk posed by open sluff combustion. The estimated emissions presented here could serve as an important data source for such an assessment. (The estimated emissions are presented in terms of mass of pollutant per mass of sluff consumed by combustion, not per mass exposed to combustion conditions.) In the interim, this document should help provide some further basis for informed decision making by personnel faced with controlling sluff fires. In particular, our data on volatiles emissions seems to confirm the suggestion previously made that the partial extinguishment of open sluff combustion processes may actually increase the total emission of pollutants.<sup>8</sup>

11. Method 5040 in Test Methods for Evaluating Solid Waste, Volume IB: Laboratory Manual Physical/Chemical Methods (Third Edition), EPA-SW-846 (NTIS PB88-239223), U.S. Environmental Protection Agency, Washington, DC, September 1986.
12. Lentzen, D.E. et al., IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), EPA-600/7-78-201 (NTIS PB293795), U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1978.
13. Wasson, S.J. and J.T. Keever, "Validation Analysis of Polynuclear Aromatic Hydrocarbons"; Technical Report No. 3967/56B-21F, May 20, 1992; Research Triangle Institute, Research Triangle Park, North Carolina.
14. Method 8280 in Test Methods for Evaluating Solid Waste, Volume IB: Laboratory Manual Physical/Chemical Methods (Third Edition), EPA-SW-846 (NTIS PB88-239223), U.S. Environmental Protection Agency, Washington, DC, September 1986.
15. Method 23 in Title 40 Code of Federal Regulations Part 60, Appendix A, U.S. Government Printing Office, Washington, DC, 1991.
16. Method 200.7 in Methods for the Determination of Metals in Environmental Samples, EPA-600/4-91/010 (NTIS PB91-231495), U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, June 1991.
17. McFarland, A.R. and C.A. Cortiz, "A 10  $\mu$ m Cutpoint Ambient Aerosol Sampling Inlet," Atmospheric Environment, 16: 2959-2965, 1982.
18. Levin, B.C., "A Summary of the NBS Literature Reviews on the Chemical Nature and Toxicity of the Pyrolysis and Combustion Products from Seven Plastics: Acrylonitrile-Butadiene-Styrenes (ABS), Nylons, Polyesters, Polyethylenes, Polystyrenes, Polyvinyl Chlorides, and Rigid Polyurethane Foams," Fire and Materials, 11, 143-157, 1987.
19. Paabo, M. and B.C. Levin, "A Literature Review of the Chemical Nature and Toxicity of the Decomposition Products of Polyethylenes," Fire and Materials, 11, 55-70, 1987.
20. Huggett, C. and B.C. Levin, "Toxicity of the Pyrolysis and Combustion Products of Polyvinylchlorides: A Literature Assessment," Fire and Materials, 11, 131-142, 1987.
21. Milera, J. and J. Michal, "The Combustion Products of Polymeric Materials," Fire and Materials, 9(3), 111-116, 1985.
22. van Wijnen, J.H., et al., "Soil Contamination with PCDDs and PCDFs of Small (Illegal) Scrap Wire and Scrap Car Incineration Sites," submitted for publication in Chemosphere.
23. Ballschmiter, K., et al., "Automobile Exhausts Versus Municipal Waste Incineration as Sources of the Polychloro-dibenzodioxins (PCDD) and -furans (PCDF) Found in the Environment," Chemosphere, 15(7), 901-915, 1986.

## APPENDIX A

### QUALITY CONTROL EVALUATION REPORT

This task was conducted under the guidance of an EPA-approved Quality Assurance Project Plan. This plan was used to establish data quality objectives suitable for this study. The quality control measures employed during this study were performed to ensure that the data collected would be suitable to collect, identify, and semi-quantitate air emissions resulting from the simulated open burning of automobile fluff. The primary project goal was to obtain qualitative information as to the types and identities of both inorganic and organic combustion by-products. The secondary goal was to provide estimate emissions accurate within an order of magnitude (factor of ten) for selected compounds and compound types identified.

Table A-1 presents the data quality indicator (DQI) summaries for accuracy, precision, and completeness achieved during testing along with the planned DQI goals for each respective measurement or analysis performed. In general, the intended DQI goals were achieved. In several instances, however, targeted DQI goals were not achieved.

Included in Table A-1 are the DQI summaries for the continuous emission monitoring systems. The performance indicators demonstrate that the systems performed well within project goals. However, operational difficulties were encountered with the total hydrocarbon analyzer and the nitric oxide analyzer. On two test days, the post-test span check for the THC analyzer exceeded established accuracy limits (Day 1: 34 percent bias, Day 2: 23 percent bias). Similarly, for the NO analyzer, the

and end of each analytical period. These QC checks were used to determine analytical method precision. Results of these QC checks are also included in Table A-1.

Table A-1 includes DQI summaries for semivolatile organic compound characterizations. The QA/QC approach to the semivolatile organic analyses was similar in nature to that of the volatile organic analyses. Once the GC/FID (TCO) and GC/MS systems were calibrated and system responses established, continuing calibration check solutions were analyzed at the beginning and end of each analytical period to evaluate system performance. The results of these QA/QC checks are also included in Table A-1.

Additional standards, containing compounds identified in test samples, were also prepared and analyzed. These standards were used to confirm tentatively identified compounds as well as to evaluate the generalized quantitative approach.

A PAH Performance Evaluation Audit (PEA) was provided by an independent QA laboratory. The sample was analyzed using the general TCO GC/FID semivolatile organic analytical method. The results of this analysis are presented in Table A-2. The results indicate that, for the PAHs identified, accuracy, expressed as percent recovery, ranged from 55-105 percent for all compounds quantified.

Three of the compounds present in the performance evaluation sample were not detected. These 3 PAHs were not detected as a result of chromatographic (temperature) limitations as opposed to detector sensitivity limitations.

Although individual analytical accuracy values for each compound identified were not determined, it is possible to estimate the accuracy of these measurements. Many of the compounds identified were quantified using both GC/MS and GC/FID system responses. The quantitative agreement between these analytical approaches were generally within a factor of two. The analytical accuracy is also supported both by the PAH PEA sample as well the TCO alkane mix accuracy performance checks which were found to exhibit less than 15 percent analytical bias. The estimated

possible to determine the molecular formula of organic unknowns, determining functional substitution groups and specific isomers often proves difficult. Similarly, the relatively low ionization potential of alkanes coupled with electron ionization (EI) makes determination of molecular ions difficult. Therefore, many of the compounds tentatively identified in this study are unable to be presented further than the molecular formula and organic class. An added emphasis was placed on using the aforementioned qualitative standards. Project resources limited further confirmatory analyses.

The metals analyses were performed by a contracted commercial laboratory. The QA/QC measures described in the respective referenced procedures were adhered to and achieved. Because many of the targeted metals were found at less than detectable levels, emission factors were also presented as less than levels based on method detection levels.

As stated earlier, PCDDs and PCDFs (tetra - octa congeners) were analyzed using a combination of techniques found in SW-846 Method 8280 and 40 CFR Part 60, Appendix A Method 23. The samples were analyzed by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS). This procedure serves to confirm the presence or absence of PCDDs and PCDFs as well as quantify the number of confirmed isomers found in each congener class. This analytical method follows the QA/QC guidelines listed in the SW-846 method. In addition, it uses isotopically labeled PCDD/PCDF homologues for each congener (with the exception of octachlorodibenzofuran). The procedure differs in that specific isomers, including the 2,3,7,8 substituted isomers, are not confirmed. Method performance is evaluated by the recovery of the isotopically labelled internal standards. The actual recovery values for each congener respective to each sample are too numerous to be included here. Table A-4 provides a summary of recovery values for each congener. In several particulate phase samples, the recovery values for several congeners were less than the targeted 40 percent. The low recoveries were not found to significantly affect data quality and were, therefore, reported.

TABLE A-2. RESULTS OF PAH PERFORMANCE EVALUATION AUDIT

COMPOUND	RECOVERY (%)
Naphthalene	92.2
Acenaphthylene	88.7
Acenaphthene	101
Fluorene	91
Phenanthrene	89.6
Anthracene	87.6
Fluoranthene	88.2
Pyrene	102.6
Chrysene	77.1
Benzo[a]anthracene	70.1
Benzo[b]fluoranthene	62.9
Benzo[k]fluoranthene	55.2
Benzo[a]pyrene	55.8
Benzo[ghi]perylene	ND
Dibenzo[a,h] anthracene	ND
Indeno[1,2,3-cd]pyrene	ND

Note: ND = Not detected

TABLE A-4. RECOVERIES OF ISOTOPICALLY LABELED PCDD/PCDF INTERNAL STANDARDS

Vapor phase samples (XAD), No. of samples and blanks in each recovery category

RECOVERY	TCDD	TCDF	PCDD	PCDF	HxCDD	HxCDF	HpCDD	HpCDF	OCDD	OCDF
40-120% (ACCEPTABLE)	5	5	5	5	5	5	5	5	5	5
< 40	0	0	0	0	0	0	0	0	0	0
> 120%	0	0	0	0	0	0	0	0	0	0

Particulate phase samples (filter), No. of samples and blanks in each recovery category

RECOVERY	TCDD	TCDF	PCDD	PCDF	HxCDD	HxCDF	HpCDD	HpCDF	OCDD	OCDF
40-120% (ACCEPTABLE)	5	4	4	5	4	5	4	4	1	1
< 40	0	1	0	0	1	0	1	1	4	4
> 120%	0	0	1	0	0	0	0	0	0	0